[CONTRIBUTIONS FROM THE CHEMICAL LABORATORIES OF THE LELAND STANFORD JUNIOR UNIVERSITY.]

POTASSIUM AMMONOSTANNATE.

By F. F. FITZGERALD.

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In former articles[1] in this Journal experiments were described which were undertaken with the object of preparing an ammonia analogue of the potassium zincate which is formed by the action of an excess of potassium hydroxide upon metallic zinc, zinc oxide or zinc hydroxide. The result of these experiments led to the present attempt to prepare other representatives of the same general class. Applying the method used successfully by Franklin in preparing pure potassium ammonozincate to a preliminary examination of the behavior of a number of metallic salts it was found that among them stannic iodide gave the most promise of success.

As is well known, stannic hydroxide is first precipitated when potassium hydroxide is added to an aqueous solution of a stannic salt to be followed, upon the addition of an excess of the precipitant, by the conversion of the stannic hydroxide into potassium stannate. If the analogous reaction takes place in ammonia, potassium amide should first cause a precipitation of stannic amide, imide or nitride, from a solution of a salt of tin in liquid ammonia, which precipitate should then, by the action of an excess of potassium amide, be changed into a potassium ammonostannate. That such a reaction takes place was found to be the case. The analogy between the reactions in the two solvents is expressed by equations such as the following :

$$SnI_4 + 4KOH = Sn(OH)_4 + 4KI$$
$$Sn(OH)_4 + 4KOH = Sn(OK)_4 + 4H_2O$$
$$SnI_4 + 4KNH_2 = Sn(NH_2)_4 + 4KI$$
$$Sn(NH_2)_4 + 4KNH_2 = Sn(NHK)_4 + 4NH_3.$$

Preparation of Potassium Ammonostannate.—The preparation of the pure compound was effected by the action of an excess of potassium amide upon absolutely water-free stannic iodide in accordance with the equation,

$$SnI_4 + 6KNH_2 = Sn(NK)_2.4NH_3 + 4KI.$$

The preparation of the potassium amide used in these experiments and the general mode of manipulation followed, are the same as described by Franklin in a former article[2]. In a number of preliminary experiments the stannic iodide used was from a specimen by Kahlbaum. Analyses of preparations made from this sample, although they approximated a definite compound, gave indications of the presence of some impurity,

[1] Fitzgerald: This Journal, **29**, 657. Franklin: Ibid., **29**, 1274.

[2] This Journal, **27**, 830.

presumably oxygen introduced as water with the stannic iodide. To avoid any possible contamination by water or other impurity, the following procedure was followed. Stannic iodide was prepared by heating a mixture of iodine and excess of metallic tin in a retort and distilling the stannic iodide thus formed, avoiding at the same time any unnecessary exposure to the air. The stannic iodide thus obtained, together with a small quantity of metallic tin was introduced through the tubulure, A, into the leg, B, of a piece of apparatus blown as represented in Figure 1.

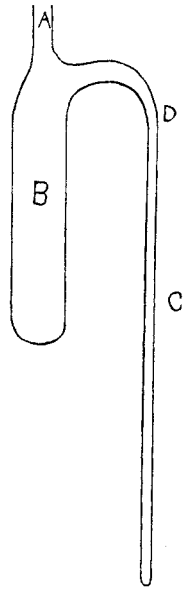

Fig. 1.

The tubulure was softened before the blowpipe, thickened and drawn down to a small diameter preliminary to sealing. The apparatus was then connected to an air pump and completely evacuated, after which the tube was sealed off at the thickened portion. By a judicious application of heat, the salt was then distilled into the leg, C, giving thus, a specimen of pure anhydrous stannic iodide since any stannous iodide or basic salt must remain behind in the leg, B. The tube, C, was then cut off at D, and its contents preserved by placing a cap over the open end of the tube. The procedure for the introduction of this stannic iodide into the reaction tube was identical with that followed for introducing pure, dry potassium.[1] When liquid ammonia is distilled into the leg containing

[1] On looking up Franklin's description ot this procedure, (This Journal, **27**, 831), the writer finds that the details are omitted. All but absolute exclusion of moisture from the reaction tube is assured by the following simple procedure. With the leg, B, Fig. 2, closed by means of a stopper and a current of ammonia gas escaping at A, the open end of the tube containing the stannic iodide is held in the escaping

the stannic iodide, the salt dissolves to a dense, colorless solution. Ammonolysis of this solution of stannic iodide is shown by the following procedure. Just sufficient ammonia is distilled into the preparation tube to dissolve the stannic iodide, solution being facilitated by shaking the tube. Then as more ammonia is distilled into the tube in such a manner as not to mix the contents, the separation of a white precipitate is observed between the layer of the concentrated solution of stannic iodide and the freshly distilled ammonia. On shaking the tube the precipitate disappears. The separation of the precipitate may be observed several times by repeating the operations above described. After a relatively large amount of liquid has been added, the precipitate becomes permanent and the separation of the tin from the solution is complete, as is shown by the fact that addition of potassium amide to the supernatant solution fails to produce any further precipitation. The addition of ammonium iodide, which, it may be remarked, acts as an acid in ammonia solution, prevents the ammonolysis of the tin salt.

On pouring a solution of potassium amide into a solution of stannic iodide a voluminous, white, precipitate of variable composition is thrown down. Analysis of this precipitate shows it to contain tin, iodine and nitrogen but not in such proportions as to indicate the formation of a definite com-

gas at A, while a small cylinder is cut from the tube of stannic iodide and rejected, thus removing the small quantity of stannic iodide contaminated by previous exposure to the air. The tube containing the stannic iodide is then introduced into the opening at A, and a cylinder of such length as desired is cut off and pushed into this leg to a distance sufficient to permit the sealing of the latter before the blow-pipe. Before proceeding

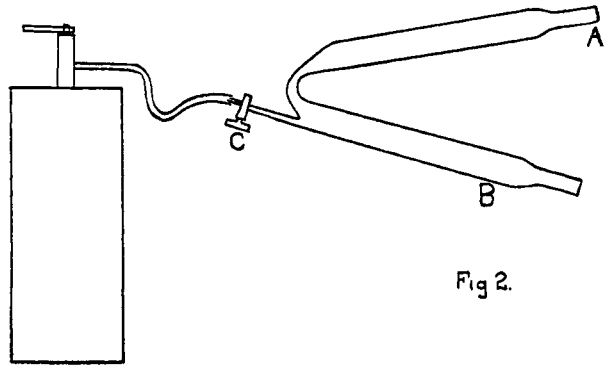

Fig 2.

to seal this leg of the reaction tube, the opening, A, is closed by means of a stopper while the leg, B, is simultaneously opened for the escape of the current of ammonia, thus excluding any possibility of accession of moisture through A during the operation of sealing. The introduction of metallic potassium into leg, B, is accomplished in the same manner, B being closed, and the stopcock plug, C, removed during the sealing of this second leg.

pound. It is therefore to be looked upon as a mixture of ammonobasic salts of tin. Addition of potassium amide in excess, changes this flocculent precipitate into a sharply crystalline product. If just sufficient potassium amide is introduced to bring about the reaction, (which can be determined by the fact that the smallest excess of the amide changes the color of the solution to a slight yellow), larger crystals are obtained than is the case when a large excess is added. The crystals of the tin salt differ in several particulars from those of the analogous zinc salt. They are formed in a few seconds after the addition of an excess of potassium amide while the zinc salt is not entirely crystalline until after the lapse of hours or days. The crystals are also much smaller than those of the zinc salt and reflect the light very beautifully while the zinc salt crystals are apparently much less dense optically.

The preparations were washed and prepared for analysis in the manner previously described.[1]

For analysis the substance was dissolved in dilute hydrochloric acid and divided into aliquot parts. In one portion the nitrogen was determined by distillation with potassium hydroxide and titration with standard acid solution. From another portion the tin was precipitated as sulphide, ignited and weighed as the oxide. The potassium contained in the filtrate from the stannic sulphide was weighed as the sulphate.

Three separate preparations gave the following results:

(I). One fourth of 0.4803 g. of substance gave 0.0344 g. nitrogen, the remaining three fourths gave 0.1861 g. stannic oxide and 0.2125 g. potassium sulphate. (II). One fourth of 0.4591 g. of the substance gave 0.0326 g. nitrogen, and 0.0592 g. stannic oxide. (III). One eighth of 1.6859 g. of the substance gave 0.0602 g. nitrogen. Three eighths of 1.6859 g. of the substance gave 0.3261 g. stannic oxide and 0.3770 g. potassium sulphate.

	Calculated for $Sn(NK)_2.4NH_3$	Found		
		I	II	III
N	28.65	28.65	28.40	28.58
Sn	40.57	40.65	40.64	40.65
K	26.70	26.50	....	26.80

Properties of the Salt.—Potassium ammonostannate is but slightly soluble in liquid ammonia but dissolves readily in a liquid ammonia solution of ammonium iodide[2]. It is also readily soluble in aqueous hydrochloric acid, the action being violent and accompanied by the evolution of much heat. It is not explosive, but if heated in contact with the air it decomposes violently and with incandescence, the heat evolved being

[1] Franklin: This Journal, 27, 830.

[2] This salt as Franklin (This Journal, 27, 822.) has pointed out acts as an acid in liquid ammonia so that the explanation of its action in this case is given by the equation, $Sn(NK)_2 + 6NH_4I \rightleftharpoons SnI_4 + 8NH_3 + 2KI$.

due to the oxidation of the tin and potassium. When heated *in vacuo* potassium ammonostannate remains unaffected up to 60°. As the temperature is increased above this point it loses ammonia.

The Compounds, $Sn(NK)_2.NH_3$ and $Sn(NK)_2.\frac{1}{2}NH_3$(?)—A specimen of potassium ammonostannate with four molecules of ammonia of crystallization was heated *in vacuo* to a maximum temperature of 145° until the evolution of ammonia ceased. 0.3578 g. of the substance lost 0.0623 g. of ammonia or 17.4 per cent. of its weight. The amount of nitrogen in the residue was found to be 0.502 g. or 17.0 per cent. The calculated loss of weight for the expulsion of three molecules of ammonia is 17.4 per cent. while the calculated content of nitrogen in the salt with one molecule of ammonia is 17.3 per cent. It therefore appears that the red residue formed by heating the compound, $Sn(NK)_2.4NH_3$, to 145° is to be assigned the formula, $Sn(NK)_2.NH_3$ or possibly $NH:Sn:(NHK)_2$.

A second specimen weighing 0.4356 g. was heated gradually up to 145°, at which temperature the evolution of ammonia ceased. The volume of ammonia given off was calculated to weigh 0.0768 g., which corresponds to 17.6 per cent., thus confirming the results of the experiment described above. As the temperature was raised to 175° an additional quantity of ammonia was given off, but even heating for hours at 316° was found insufficient to drive off all the ammonia. The final product approximated in composition the formula, $Sn(NK)_2.\frac{1}{2}NH_3$, as is shown by the following analytical data. The total loss of ammonia from 0.4356 g. of the original substance was 0.0835 g., corresponding to 19.0 per cent. The calculated loss for three and one-half molecules is 20.3 per cent. In the residue 0.0542 g. of nitrogen was found, corresponding to 12.4 per cent. while the amount calculated for the compound with half a molecule of ammonia is 11.9 per cent. The existence of a compound $Sn(NK)_2.\frac{1}{2}NH_3$. requires confirmation.

The final product obtained by heating the original compound is a brick red powder which remains unfused at a temperature of 316°. On allowing water to enter the tube, but in such a manner that the liquid does not come in contact with the substance, the latter is rapidly acted upon by the water vapor and is changed into a white mass which dissolves readily and completely in aqueous hydrochloric acid. When liquid water was allowed to come into contact with the red powder, violent action followed, resulting in the deposition of a metallic mirror on walls of the tube and the separation of a quantity of gas. The metallic mirror dissolved in hydrochloric acid with the evolution of gas and consequently must have been metallic tin. The gases formed during the decomposition of the salt were not identified, but it is not obvious how the separation of tin and gas by the action of water is to be explained other than by the assump-

tion that a portion of the salt was decomposed in accordance with the equation,

$$Sn(NK)_2 + 2H_2O = Sn + N_2 + H_2 + 2KOH.$$

This partial decomposition is to be ascribed to the violence of the action of liquid water and the high temperature thereby produced. The hydrolytic action of the water vapor is to be represented by the equation,

$$Sn(NK)_2 + 6H_2O = Sn(OH)_4 + 2KOH + 2NH_3.$$

Summary of Results.

It is shown by the work described above that a potassium ammonostannate of the formula, $Sn(NK)_2.4NH_3$, $(NH_2)_2:Sn:(NHK)_2.2NH_3$, $(KHN)_2:Sn:(NHNH_4)_2$ or $Sn(NH_2)_4.2KNH_2$, an ammonia analogue of potassium stannate, is formed when a solution in liquid ammonia of potassium amide in excess is allowed to act upon stannic iodide, likewise in solution in liquid ammonia, and that this compound, when heated to a temperature not in excess of 145°, loses three molecules of ammonia of crystallization to form the compound, $Sn(NK)_2.NH_3$ or $HN:Sn:(NHK)_2$. From this compound even by heating for several hours *in vacuo* to 316° it was not possible to obtain the ammonia-free salt.

The writer is under obligations to Dr. E. C. Franklin of Stanford University for his many suggestions and great assistance in carrying on this investigation.

STANFORD UNIVERSITY,
California, *Summer* 1907.

[CONTRIBUTION FROM KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO.]

THE SPECIFIC RADIOACTIVITY OF URANIUM.[1]

BY HERBERT N. MCCOY AND W. H. ROSS.

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It may be considered as fully established[2] that the specific activity of Uranium in any pure uranium compound or in any uranium mineral, free from thorium, is in either case strictly constant. The value of these constants has been given as 790 for pure compounds and 3280 for minerals. These values were obtained from activity measurements made with a distance of 3.5 to 4.5 cm. between the active film and the charged electrode of the gold leaf system. It is now known[3] that the ranges of RaA and RaC both exceed 4.5 cm.; for which reason the value given for the specific activity of uranium in a mineral is too low. New measurements have now been made by means of a new improved gold-leaf electroscope which has an ionization chamber 19.5 cm. square and allows a distance of 8.5 cm. between the active films and the superimposed

[1] Read, in abstract, before the Amer. Phys. Soc., Chicago, Dec. 1, 1906; Phys. Rev., Jan., 1907.

[2] McCoy, Ber., 37, 2641 (1904); This Journal, 27, 391 (1905); Phil. Mag., 11, 176 (1906); Goettsch, This Journal, 28, 1541 (1906).

[3] Bragg and Kleeman, Phil. Mag., 10, 318 (1905).